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Mechanistic Study of the Carbonylation of Nitrobenzene Catalyzed by the $[Rh(CO)_4]^-$/Nitrogen Base System. X-ray Structure of $[PPN][Rh(CO)_2ON(C_6H_3Cl_2)C(O)O]$

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$[PPN][Rh(CO)_4]$ (**1**) reacts with $ArNO_2$ or ArNO to yield the same product (Ar = Ph, **2**; Ar = 3,4-Cl_2-C_6H_3, **3**). The reaction of **1** with nitrosoarenes also produces the corresponding azoxyarenes. The product was structurally characterized in the case of Ar = 3,4-dichlorophenyl and was shown to be $[PPN][Rh(CO)_2ON(C_6H_3Cl_2)C(O)O]$ (**3**). Crystal data for **3**: $C_{45}H_{33}Cl_2N_2O_5P_2Rh\cdot C_4H_8O$, $M_r = 989.64$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.798(4)$ Å, $b = 9.889(6)$ Å, $c = 21.648(6)$ Å, $\alpha = 89.77(1)°$, $\beta = 96.00(1)°$, $\gamma = 92.71(1)°$, $V = 2296(2)$ Å^2, $Z = 2$, $D_c = 1.431$ g cm^{-3}, Mo Kα radiation ($\lambda = 0.710\,73$ Å), μ(Mo Kα) = 6.00 cm^{-1}, $R = 0.037$ ($R_w = 0.047$) for 5299 independent reflections having $I > 3\sigma(I)$. Both of the reactions proceed through electron transfer to the nitroso or nitro derivative. Reaction of **2** and **3** with MeOH and CO produced the corresponding amine or the methyl carbamate, depending on the experimental conditions. The reaction of **3** with MeOH/CO was faster in the presence of nitrogen bases, and aniline was shown to be an intermediate in the synthesis of the carbamate. When the same reaction was performed in the presence of a large excess of nitrosobenzene, the two isomeric mixed azoxybenzenes 3,4-Cl_2-$C_6H_3N(O)$=NPh and 3,4-Cl_2-C_6H_3N=N(O)Ph were the largely dominant products, which strongly suggests the intermediate formation of a nitrene complex.

Introduction

Carbonylation of organic nitro compounds is a reaction of high potential synthetic and industrial interest, since many products can be obtained from nitro compounds and CO in a single step, including amides, amines, oximes, ureas, carbamates, isocyanates, and indoles.[1] Ureas and carbamates are important final products and intermediates in the synthesis of pesticides and fertilizers, and mono- and diisocyanates are important intermediates in the manufacturing of pesticides, polyurethane foam plastics, synthetic leather, adhesives, and coatings.

The classical method for producing isocyanates requires the intermediate reduction of a nitro compound to the corresponding amine, followed by reaction with phosgene. However, phosgene is a very toxic and corrosive material, and an enormous effort has been applied to the development of phosgene-free routes to isocyanates. Among these, the carbonylation of nitro compounds, particularly aromatic ones, represents one of the more interesting alternatives, but the direct carbonylation of nitro compounds to the corresponding isocyanates has proved to be a difficult reaction. However, in the presence of an alcohol, carbamates can be obtained more easily with high selectivity (eq 1).

$$RNO_2 + R'OH + 3CO \rightarrow RNHCOOR' + 2CO_2 \quad (1)$$

If the isocyanate is the desired product, this can be obtained (at least for R = aryl) by thermal cracking of the carbamate (eq 2).

$$RNHCOOR' \xrightarrow{\Delta} RNCO + R'OH \quad (2)$$

Recently, Liu and Cheng[2] and some of us[3] independently reported the use of $[PPN][Rh(CO)_4]$ (**1**; $PPN^+ = (PPh_3)_2N^+$) as a catalyst for the carbonylation of nitrobenzene to alkyl phenylcarbamates. We also found that bpy (2,2′-bipyridyl) is a good cocatalyst for this reaction. The main byproducts were aniline and azoxybenzene, although trace amounts of azobenzene were also present. The amount of azoxybenzene produced was highly dependent on the concentration of nitrobenzene in the catalytic solution, and none was formed at low concentrations.[3]

In this paper we report the results of a mechanistic study on this catalytic system. A preliminary account of part of this work has been published.[4]

Results and Discussion

Reactions of $[PPN][Rh(CO)_4]$ (1) with bpy, $ArNO_2$, and ArNO. We first checked the possible reaction of **1** with bpy to afford a complex such as $[PPN][Rh(CO)_2(bpy)]$. No reaction was observed in refluxing THF or

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[1] Cenini, S.; Pizzotti, M.; Crotti, C. Metal Catalyzed Deoxygenation Reactions by Carbon Monoxide of Nitroso and Nitro Compounds. In *Aspects of Homogeneous Catalysis*; Ugo, R., Ed.; D. Reidel: Dordrecht, The Netherlands, 1988; Vol. 6, pp 97–198.

[2] Liu, C.; Cheng, C. *J. Organomet. Chem.* **1991**, *420*, 119.

[3] Ragaini, F.; Cenini, S.; Fumagalli, A.; Crotti, C. *J. Organomet. Chem.* **1991**, *428*, 401.

[4] Ragaini, F.; Cenini, S.; Demartin, F. *J. Chem. Soc., Chem. Commun.* **1992**, 1467.

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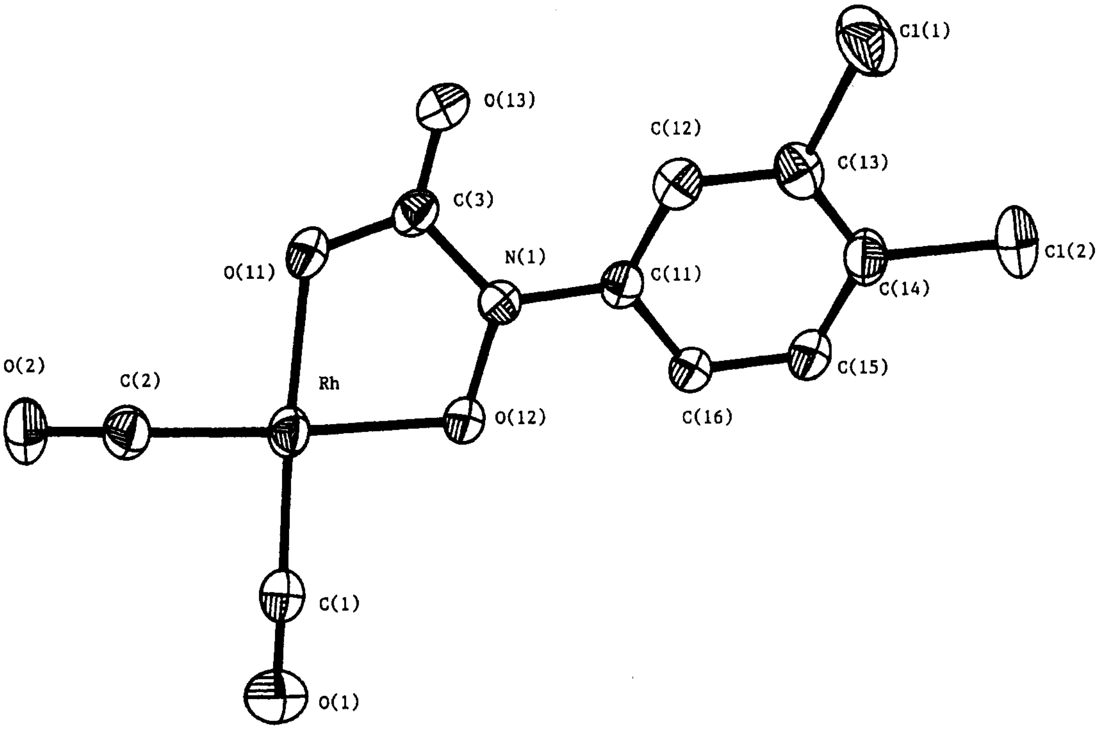

Figure 1. Ortep view of the $[\overline{Rh(CO)_2ON(C_6H_3Cl_2)C(O)O}]^-$ anion. Thermal ellipsoids are drawn at 30% probability.

acetone, whereas rhodium metal and $[RhCl_2(CO)_2]^-$ were respectively formed in refluxing toluene and dichlorobenzene.[5] Under the same conditions used in catalytic reactions (200 °C, P_{CO} = 60 atm, THF), some as yet unidentified compounds (probably cluster complexes) were formed, but they reacted with nitrobenzene much more slowly than did 1 and cannot be intermediates in the catalytic cycle.

As it seems possible to exclude the direct interaction of 1 by bpy, we examined the reaction between 1 and nitrobenzene. A smooth reaction was observed at 40 °C, affording a complex (2) showing three bands in the IR spectrum at 2045 (s), 1967 (vs), and 1635 (m) cm^{-1} (THF). The same product was obtained by the use of nitrosobenzene in place of nitrobenzene, but 3 equiv of nitrosobenzene was necessary and azoxybenzene was also formed.[6] The reaction with nitrosobenzene was much faster and was complete in less than 3 min at room temperature. The use of smaller amounts of nitrosobenzene gave the same product together with unreacted 1. No intermediate was observable by IR spectroscopy during either of these two reactions.

Unfortunately, 2 was not stable enough to allow purification, but an analogous, more stable complex (3) was obtained by use of 3,4-dichloro-1-nitrobenzene, and its structure was solved by X-ray diffraction (Figure 1). The nitro group of the starting organic compound has been reduced to a nitroso moiety by a coordinated CO, but the CO_2 molecule thus resulting has not left the coordination sphere of the metal. It should be noted that CO_2 has surely rearranged from its original position, in which the carbon atom was necessarily bound to rhodium. This is the first time that a metallacycle of this kind has been observed during a deoxygenation reaction of nitrobenzene, although two similar metallacycles have been previously obtained by reaction of CO_2 with nitroso complexes.[7,8] In the present case, however, the possibility that CO_2 is delivered into the solution and then taken up again can be excluded, since no appreciable variation in the outcome of the reaction was observed when nitrogen was vigorously bubbled through the solution during the reaction.

Crystallographic details and selected interatomic distances and angles within the $[\overline{Rh(CO)_2ON(C_6H_3Cl_2)C(O)O}]^-$ anion of 3 are reported in Tables 1–3. A perspective view of the anion is shown in Figure 1. Crystals of compound 3 contain PPN^+ cations, $[\overline{Rh(CO)_2ON(C_6H_3Cl_2)C(O)O}]^-$ anions, and THF molecules packed in the crystal lattice in the molar ratio 1:1:1; interionic and intermolecular contacts are not shorter than the normal van der Waals interactions. The rhodium atom displays the expected square-planar coordination. Displacements (Å) from the average coordination plane are as follows: C(1), −0.044(5); C(2), 0.044(5); O(11), −0.043(3); O(12), 0.044(3). Also, the metallacycle is slightly folded with the following deviations (Å) from the average

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(5) In our first paper on this topic,[3] we tentatively formulated the product of the reaction of 1 with bpy in dichlorobenzene as $[Rh(CO)_2(bpy)]$. However we later discovered, as reported here, that this complex was indeed $[RhCl_2(CO)_2]^-$. Therefore, the original proposal must be considered erroneous. Also, the previously reported reaction of this complex with nitrobenzene, to yield a still uncharacterized compound, is a reaction of $[RhCl_2(CO)_2]^-$.

(6) An additional small absorption of varying intensity at 1672 cm^{-1} in the IR spectrum of the reaction mixture was observed when nitrosobenzene or other nitrosoarenes were used as starting materials. When excess ArNO was added to our reaction mixture, the absorption did not disappear. Therefore, it cannot be attributed to any intermediate in the formation of 2. In our first paper on this topic,[3] we reported that two different products (at that time both uncharacterized) were formed by reaction of 1 with nitroso- and nitrobenzene. The products were considered to be different on the basis of slightly different IR spectra recorded on an old IR spectrophotometer. However, when the same reactions were examined using the more precise and reproducible FT-IR spectrophotometer used in the course of this study, the two product spectra were identical. Additional evidence for the identity of the products of the two reactions comes from their mass spectra (*vide infra*).

(7) Cenini, S.; Porta, F.; Pizzotti, M.; Crotti, C. *J. Chem. Soc., Dalton Trans.* **1985**, 163.

(8) Dahlenburg, L.; Prengel, C. *Inorg. Chim. Acta* **1986**, *122*, 55.

Table 1. Crystal Data for $[PPN][\overline{Rh(CO)_2ON(C_6H_3Cl_2)C(O)O}]\cdot C_4H_8O$ (3)

formula	$C_{45}H_{33}Cl_2N_2O_5P_2Rh\cdot C_4H_8O$
fw	989.64
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	10.798(4)
b (Å)	9.889(6)
c (Å)	21.648(6)
α (deg)	89.77(1)
β (deg)	96.00(1)
γ (deg)	92.71(1)
V (Å^3)	2296(2)
Z	2
D_{calc} (g cm^{-3})	1.431
μ (cm^{-1})	6.00
min transmissn factor	0.93
scan mode	ω
ω scan width (deg)	$1.3 + 0.35 \tan\theta$
θ range (deg)	1–25
reciprocal space explored	$+h,\pm k,\pm l$
no. of measd rflns	8055
no. of unique obsd rflns with $I > 3\sigma(I)$	5299
final R and R_w indices[a]	0.037, 0.047
no. of variables	559
GOF[b]	1.495

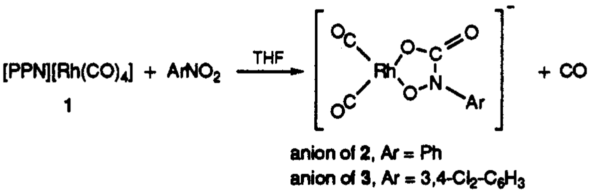
[a] $R = [\Sigma(F_o - k|F_c|)/\Sigma F_o]$; $R_w = [\Sigma w(F_o - k|F_c|)^2/\Sigma wF_o^2]^{1/2}$. [b] GOF $= [\Sigma w(F_o - k|F_c|)^2/(N_{observations} - N_{variables})]^{1/2}$: $w = 1/(\sigma(F_o))^2$, $\sigma(F_o) = [\sigma^2(I) + (0.04I)^2]^{1/2}/2F_oLp$.

Table 2. Fractional Atomic Coordinates for $[PPN][\overline{Rh(CO)_2ON(C_6H_3Cl_2)C(O)O}]\cdot C_4H_8O$ (3)

atom	x	y	z
Rh	0.38214(3)	0.14715(4)	0.11264(2)
Cl(1)	0.3830(2)	−0.1109(2)	0.45657(6)
Cl(2)	0.0901(1)	−0.0824(2)	0.45082(6)
P(1)	−0.13366(8)	0.32860(9)	0.19726(4)
P(2)	0.06701(9)	0.5453(1)	0.21839(4)
O(1)	0.2245(4)	0.3591(5)	0.0550(2)
O(2)	0.5307(3)	0.1753(4)	0.0052(2)
O(11)	0.4895(2)	0.0111(3)	0.1583(1)
O(12)	0.2848(3)	0.1111(3)	0.1845(1)
O(13)	0.5141(3)	−0.1062(4)	0.2468(2)
N	−0.0012(3)	0.4041(3)	0.2012(2)
N(1)	0.3527(3)	0.0323(3)	0.2285(2)
C(1)	0.2827(5)	0.2759(6)	0.0769(2)
C(2)	0.4741(4)	0.1664(5)	0.0465(2)
C(3)	0.4585(4)	−0.0266(4)	0.2124(2)
C(11)	0.2925(4)	0.0021(4)	0.2815(2)
C(12)	0.3579(4)	−0.0376(4)	0.3368(2)
C(13)	0.2965(4)	−0.0631(4)	0.3883(2)
C(14)	0.1694(4)	−0.0496(5)	0.3864(2)
C(15)	0.1035(4)	−0.0123(5)	0.3312(2)
C(16)	0.1644(4)	0.0157(4)	0.2796(2)
C(111)	−0.1280(3)	0.1836(4)	0.1482(2)
C(112)	−0.0157(4)	0.1498(4)	0.1278(2)
C(113)	−0.0114(4)	0.0357(5)	0.0910(2)
C(114)	−0.1170(5)	−0.0446(4)	0.0755(2)
C(115)	−0.2285(4)	−0.0126(4)	0.0952(2)
C(116)	−0.2348(4)	0.1015(4)	0.1320(2)
C(121)	−0.1731(3)	0.2689(4)	0.2719(2)
C(122)	−0.0836(4)	0.2742(5)	0.3224(2)
C(123)	−0.1132(5)	0.2268(6)	0.3793(2)
C(124)	−0.2312(5)	0.1764(5)	0.3864(2)
C(125)	−0.3201(4)	0.1703(5)	0.3367(2)
C(126)	−0.2924(4)	0.2170(5)	0.2795(2)
C(131)	−0.2608(3)	0.4276(4)	0.1652(2)
C(132)	−0.2877(4)	0.4371(4)	0.1013(2)
C(133)	−0.3758(5)	0.5239(6)	0.0766(2)
C(134)	−0.4395(5)	0.5984(6)	0.1144(3)
C(135)	−0.4138(5)	0.5911(5)	0.1779(3)
C(136)	−0.3248(4)	0.5058(5)	0.2032(2)
C(211)	0.2104(3)	0.5179(4)	0.2655(2)
C(212)	0.2725(4)	0.6189(4)	0.3024(2)
C(213)	0.3884(4)	0.5975(5)	0.3329(2)
C(214)	0.4438(4)	0.4760(5)	0.3270(2)
C(215)	0.3829(4)	0.3753(5)	0.2905(2)
C(216)	0.2657(4)	0.3954(4)	0.2597(2)
C(221)	0.1086(3)	0.6289(4)	0.1490(2)
C(222)	0.2116(4)	0.7201(4)	0.1503(2)
C(223)	0.2431(4)	0.7804(4)	0.0964(2)
C(224)	0.1727(4)	0.7543(4)	0.0408(2)
C(225)	0.0701(4)	0.6657(5)	0.0389(2)
C(226)	0.0386(4)	0.6022(4)	0.0928(2)
C(231)	−0.0255(4)	0.6563(4)	0.2583(2)
C(232)	−0.0408(4)	0.6329(5)	0.3203(2)
C(233)	−0.1281(5)	0.7040(6)	0.3480(2)
C(234)	−0.1993(5)	0.7956(5)	0.3145(3)
C(235)	−0.1827(5)	0.8210(5)	0.2543(3)
C(236)	−0.0960(4)	0.7520(4)	0.2255(2)
C(900)	0.234(1)	0.299(1)	0.4612(6)
O(901)	0.1463(8)	0.387(1)	0.4625(5)
C(902)	0.1845(9)	0.501(1)	0.4804(5)
C(903)	0.3027(8)	0.493(1)	0.5152(5)
C(904)	0.3430(8)	0.358(1)	0.5068(6)

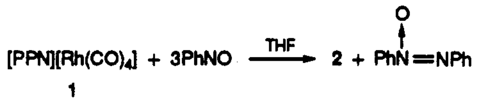
plane: Rh, −0.048(1); O(11), 0.040(3); O(12), 0.069(3); N(1), −0.061(3); C(3), 0.000(4). The C(11–16) phenyl ring is twisted about the N(1)–C(11) bond with respect to the metallacycle plane, with a C(3)–N(1)–C(11)–C(12) torsion angle of 32°. The pattern of bond distances of the metallacycle and neighbor atoms is indicative of a predominant double-bond character for the C(3)–O(13) interaction and of delocalized π electron density through the remaining atoms.

The reactions of nitro- and nitrosoarenes with 1 can be now written as shown in eqs 3 and 4.



(3)

anion of 2, Ar = Ph
anion of 3, Ar = 3,4-Cl$_2$-C$_6$H$_3$


$$[PPN][Rh(CO)_4] + 3PhNO \xrightarrow{THF} 2 + Ph\overset{\overset{O}{\uparrow}}{N}{=}NPh \quad (4)$$

1

Reactions 3 and 4 can be performed under either a dinitrogen or CO atmosphere, but yields were consistently higher in the latter case. Despite the fact that 2 and 3 are the only carbonyl-containing products observed (see, however, ref 6), some dark material was also formed during the reactions.

Reactions 3 and 4 both proceed through an intermediate electron transfer from 1 to the nitro or nitroso compound. This was evidenced by performing reaction 4 (employing a large excess of nitrosobenzene) inside an EPR tube, equipped with a side reservoir which allowed mixing of the reagents just before recording the spectra. Such a reaction gave a strong EPR signal at room temperature that is attributed to the radical anion of nitrosobenzene dimer on the basis of the typical 45-line splitting (a triplet, J_t = 14.4 G, split into quintuplets, J_q = 3.0 G, split into triplets, J_t = 1.0 G) previously reported in the literature.[9] No ESR signal could be observed when reaction 3 was performed with nitrobenzene, probably because the reaction is too slow at room temperature. However, a strong signal was immediately apparent when 3,4-dichloronitrobenzene was employed. The splitting could be best resolved by cooling the solution to 0 °C 2 min after mixing of the reagents, and the signal consists of a 1:1:1 triplet (J_t = 8.8 G) split into doublets (J_d = 3.9 G). This splitting is clearly indicative of a nitrogen-centered radical. How-

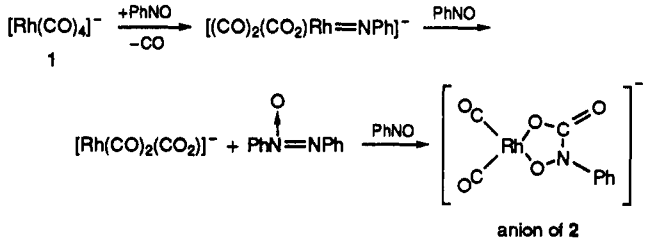
Table 3. Selected Interatomic Distances (Å) and Angles (deg) for [PPN][Rh(CO)$_2$ON(C$_6$H$_3$Cl$_2$)C(O)O]·C$_4$H$_8$O (3)

Rh–O(11)	2.008(2)	O(13)–C(3)	1.218(4)
Rh–O(12)	1.989(2)	N(1)–C(3)	1.384(4)
Rh–C(1)	1.822(5)	N(1)–C(11)	1.401(4)
Rh–C(2)	1.830(4)	C(11)–C(12)	1.390(5)
Cl(1)–C(13)	1.739(4)	C(11)–C(16)	1.392(5)
Cl(2)–C(14)	1.734(4)	C(12)–C(13)	1.372(5)
O(1)–C(1)	1.132(5)	C(13)–C(14)	1.381(5)
O(2)–C(2)	1.136(4)	C(14)–C(15)	1.383(5)
O(11)–C(3)	1.299(4)	C(15)–C(16)	1.376(5)
O(12)–N(1)	1.398(3)		
O(11)–Rh–O(12)	80.44(9)	O(11)–C(3)–N(1)	113.6(3)
O(11)–Rh–C(1)	175.6(2)	O(13)–C(3)–N(1)	121.4(3)
O(11)–Rh–C(2)	96.1(1)	N(1)–C(11)–C(12)	121.7(3)
O(12)–Rh–C(1)	96.1(1)	N(1)–C(11)–C(16)	119.5(3)
O(12)–Rh–C(2)	175.6(2)	C(12)–C(11)–C(16)	118.8(3)
C(1)–Rh–C(2)	87.5(2)	C(11)–C(12)–C(13)	120.2(3)
Rh–O(11)–C(3)	116.3(2)	Cl(1)–C(13)–C(12)	118.4(3)
Rh–O(12)–N(1)	109.8(2)	Cl(1)–C(13)–C(14)	120.7(3)
O(12)–N(1)–C(3)	118.8(3)	C(12)–C(13)–C(14)	120.9(4)
O(12)–N(1)–C(11)	114.4(3)	Cl(2)–C(14)–C(13)	121.6(3)
C(3)–N(1)–C(11)	125.8(3)	Cl(2)–C(14)–C(15)	119.3(3)
Rh–C(1)–O(1)	177.5(5)	C(13)–C(14)–C(15)	119.1(3)
Rh–C(2)–O(2)	178.5(4)	C(14)–C(15)–C(16)	120.4(4)
O(11)–C(3)–O(13)	125.1(3)	C(11)–C(16)–C(15)	120.5(3)

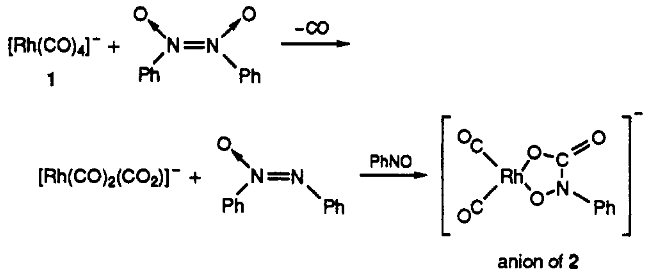
ever, we do not feel confident in assigning it to any specific species. The signal is different from the one we observed for the radical anion of 3,4-dichloronitrobenzene, which was formed by reaction of 3,4-dichloronitrobenzene with metallic potassium. Reaction 3 is several orders of magnitude faster when 3,4-dichloronitrobenzene is used in place of simple nitrobenzene. This fact, together with the absence of any IR-detectable intermediate in both cases, suggests that the slow step of reaction 3 is an *outer-sphere* electron transfer.[11]

Electron transfer from a metal complex to nitro or nitroso aromatic compounds has been previously reported in two other cases,[12] and indirect evidence for its occurrence has been given for a third system.[13] To the best of our knowledge, these are also the only cases in which experiments have been conducted to detect it. Thus, the formation of radicals is probably a more general phenomenon in reactions of this type.

Scheme 1



Scheme 2



The formation of the metallcycle 2 from nitrosobenzene, with the concomitant formation of azoxybenzene (eq 4), deserves more comment. Catalytic deoxygenation of nitrosobenzene to afford azoxybenzene has already been reported to be catalyzed by rhodium[14] or ruthenium[15] complexes. In the case of rhodium, a nitrene complex was suggested as an intermediate. Such a complex may also be formed in the present case when nitrosobenzene is used as a starting material (Scheme 1). However, since nitrosobenzene is in equilibrium in solution with its dimeric form and 1 is known to deoxygenate even simple azoxybenzene, albeit at higher temperatures,[3] another possibility must be considered (Scheme 2). When reaction 4 was performed in the presence of a large excess of methanol, however, only 1 equiv of nitrosobenzene was necessary to consume all of 1, and aniline was the largely dominant product. Since only a trace of azoxybenzene was formed,[16] the mechanism in Scheme 2 can be excluded, while the intermediate formation of a nitrene complex is supported. It should be noted that although we have consistently represented the intermediate complex as having independent nitrene and CO$_2$ groups and have referred to it as a nitrene complex throughout this paper, we cannot exclude for this compound a metallacyclic structure such as

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(9) (a) Ginzburg, V. A.; Medvedev, A. N.; Dubov, S. S.; Lebedeva, M. F. *Dokl. Akad. Nauk SSSR* **1966**, *167*, 1083; *Dokl. Phys. Chem. (Engl. Transl.)* **1966**, *167*, 223. (b) The signal was observable for a much longer time (1 h) than the typical reaction time scale (<3 min). Thus, this signal is derived from some monomeric nitrosobenzene radical which has been trapped by free nitrosobenzene and has escaped further reaction with the rhodium complex. Given the high sensitivity of the EPR technique, it may be argued that what we are observing is indeed only a side reaction and that the main reaction course does not involve radicals. Two facts must be considered which contradict this objection. First, the reaction with 3,4-dichloronitrobenzene is orders of magnitude faster than the reaction of simple nitrobenzene (see Experimental Section) and the reaction with nitrosobenzene is even faster (*vide infra*). Nitrosobenzene is known to be reduced at potentials less negative than for nitrobenzene,[10] and the same is obviously true for the dichloro derivative. Moreover, the isolated yield increased from 21% to as much as 75% (in the case of 3,4-dichloro-1-nitrobenzene) when the reaction was performed under a CO rather than a N$_2$ atmosphere, despite the fact that no additional CO is required by the stoichiometry of the reaction and that 1 equiv of CO is actually formed during it. Our data (see later) suggest that the other product of the initial electron transfer is [Rh(CO)$_4$]$^•$, which, as for most 17 e$^-$ organometallic species, is expected to be very labile. It may lose CO to give unsaturated species which would aggregate, finally affording the black, non-carbonyl-containing solid. A CO atmosphere is thought to prevent this last process. Both of these observations are consistent with a radical path involving all the reacting molecules, or at least most of them, but would be difficult to explain otherwise.

(10) Holleck, L.; Schindler, R. *Z. Elektrochem.* **1956**, *60*, 1138.

(11) An *inner-sphere* electron transfer would require the intermediate formation of [Rh(CO)$_3$(ArNO$_2$)]$^-$ (A). Three possibilities exist for the kinetics of the reaction if this intermediate were formed: (a) The formation of A proceeds through a dissociative pathway and loss of CO from [Rh(CO)$_4$]$^-$ is rate determining in the synthesis of 2 and 3. (b) The rate-determining step involves attack of ArNO$_2$ on either [Rh(CO)$_4$]$^-$ or [Rh(CO)$_3$]$^-$. (c) The electron transfer is rate determining. If (a) were correct, the reaction of PhNO$_2$ and 3,4-Cl$_2$-C$_6$H$_3$NO$_2$ should proceed at the same rate. If (b) were correct, the more basic PhNO$_2$ should react faster than 3,4-Cl$_2$-C$_6$H$_3$NO$_2$. If (c) were correct, A should be observable in solution by IR, at least for Ar = Ph. None of these is consistent with what is experimentally found.

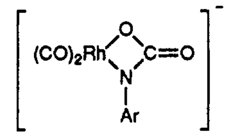
(12) (a) Sherlock, S. J.; Boyd, D. C.; Moasser, B.; Gladfelter, W. L. *Inorg. Chem.* **1991**, *30*, 3626. (b) Kunin, A. J.; Noirot, M. D.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1989**, *111*, 2739. (c) Belousov, Y. A.; Kolosova, T. A. *Polyhedron* **1987**, *6*, 1959.

(13) Berman, R. S.; Kochi, J. K. *Inorg. Chem.* **1980**, *19*, 248.

(14) Vasapollo, G.; Nobile, C. F.; Giannoccaro, P.; Allegretta, F. *J. Organomet. Chem.* **1984**, *277*, 417.

(15) Porta, F.; Pizzotti, M.; Cenini, S. *J. Organomet. Chem.* **1981**, *222*, 279.

(16) (a) During the reaction 2 was not formed, but a cluster compound showing an IR absorption pattern closely resembling that of [NMe$_4$][Rh$_{11}$(CO)$_{23}$][16b] was observed. This last cluster is often obtained after oxidative decomposition of 1. (b) Fumagalli, A.; Martinengo, S.; Ciani, G.; Sironi, A.; Heaton, B. T. *J. Chem. Soc., Dalton Trans.* **1988**, 163.



Complexes having this structure have been isolated for Mo, W, Re, and Ir.[17] However, no reaction between these latter complexes and nitroso compounds has been reported. The metallacyclic structure and the structure having independent nitrene and CO_2 moieties may also correspond to two different complexes in equilibrium. In this case the nitrene–CO_2 isomer would more likely be responsible for further reactions.[18,19] Additional evidence for the formation of nitrene species even during the catalytic cycle is reported later in this paper.

Reactivity of $[PPN][Rh(CO)_2ON(C_6H_3Cl_2)C(O)O]$ (3) with MeOH/CO. Once formed, 3 is relatively stable and does not show any tendency to lose CO_2. Heating at 60 °C in THF is necessary to observe a reaction, and the products are a trace amount of 3,4-dichloroaniline and an as yet unidentified insoluble material. No simple nitroso complex is observed in solution during the reaction.[20]

In contrast, compound 3 reacts with methanol at room temperature and atmospheric CO pressure to afford 3,4-dichloroaniline and regenerate 1 (eq 5). The regeneration

$$3 \xrightarrow[\text{CO}]{\text{THF/MeOH}} 3,4\text{-}Cl_2\text{-}C_6H_3NH_2 + 1 + CO_2 \qquad (5)$$

of 1 is an important point, as it indicates that 1 is actually a part of the catalytic cycle and is not only a catalyst precursor. The reaction is faster if bpy or even pyridine is added to the solution, but at the end of the reaction, only 1 is formed in every case. No appreciable difference in the rate of decomposition of the metallacycle was observed if bpy or a double molar amount of pyridine was added. Thus, bpy is apparently acting only as a base, and its chelating nature is not influential. Pyridine, *N*-methylimidazole, and triethylamine were also comparable to bpy (when added in double molar amount) even when used as promoters in the catalytic carbonylation of nitrobenzene to methyl phenylcarbamate. This was unexpected, since we found that pyridine is completely ineffective as a promoter when $Rh_4(CO)_{12}$ is used as a catalyst precursor instead of 1, whereas bpy strongly promotes the activity of this last cluster.[21] The results of the catalytic reactions are collected in Table 4. The virtually indistinguishable promoting activities of triethylamine and pyridine were also unexpected. The former is a much poorer ligand than the second for low-valent transition-metal complexes for both electronic and steric reasons. Their comparable activities further support the idea that the nitrogen base is functioning only as a base and does not influence the reaction by coordinating to the metal. This is at variance with what is observed, or simply proposed, for almost any of the large number of catalytic processes in which pyridine or similar nitrogen bases are used as promoters. Studies are in progress to ascertain the reasons for the different behavior of bpy and pyridine with respect to 1 and $Rh_4(CO)_{12}$, and the results will be reported elsewhere.

Table 4. Carbonylation of Nitrobenzene, Catalyzed by $[PPN][Rh(CO)_4]$ (1) or $Rh_4(CO)_{12}$ and Nitrogen Bases[a]

catalyst	base	conversion (%)[b]	select. carbamate (%)[c]	select. aniline (%)[c]
1	bpy	65.0	74.5	10.5
1	pyridine	63.5	76.3	9.6
1	Me-imidazole	62.2	79.7	10.3
1	Et_3N	66.1	73.1	8.5
$Rh_4(CO)_{12}$	pyridine	~3		*d*

[a] Conditions: [Rh] = 0.125 M; molar ratios [Rh]/base/$PhNO_2$ = 1/3/300 for bpy and 1/6/300 for the other bases; T = 200 °C, P_{CO} = 60 atm; in toluene (8 mL) + MeOH (3 mL) for 1.5 h. Small amounts of azo- and azoxybenzene were also always detected. [b] Calculated with respect to the starting nitrobenzene. [c] Calculated with respect to the converted nitrobenzene. [d] A trace amount of aniline, but no carbamate, was detected.

The absence of carbamate among the products of the reaction run under atmospheric CO pressure is not surprising, since carbamates are usually formed only under high CO pressure and at high temperature. In fact, when an impure sample of 2 was added, by means of a high-pressure side reservoir, to a THF–MeOH solution preheated at 200 °C and under 60 atm of CO, carbamate was formed along with aniline.

Compound 3 reacted with bpy in THF only very slowly to afford 3,4-dichloroaniline and an as yet unidentified insoluble material. Thus, the rate enhancement caused by bpy in the reaction with methanol cannot be due to a direct interaction between bpy and 3 (either coordination or attack on a ligand) before the interaction with methanol.

The reaction of 3 to afford 3,4-dichloroaniline requires a source of hydrogen. The necessary hydrogen atoms may be derived from only the hydroxylic protons of the added methanol or from dehydrogenation of the alcohol, through β-hydrogen elimination from a methoxy complex. In order to resolve this issue, we repeated reaction 5 using an alcohol which cannot undergo dehydrogenation. Although ^{t}BuOH gave a very sluggish reaction, accompanied by extensive decomposition, *p*-cresol gave a fast reaction, to yield as a primary product a complex showing two absorptions in the IR spectrum in the terminal carbonyl region at 2047 (s) and 1973 (s) cm^{-1}, indicative of a *cis*-dicarbonyl complex. Also formed was 3,4-dichloroaniline. This intermediate

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[17] (a) Jernakoff, P.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1610. (b) Kustard, U.; Hermann, W. A.; Ziegler, M. L.; Zahn, T.; Nuber, B. *J. Organomet. Chem.* **1986**, *311*, 163. (c) Glueck, D. S.; Wu, J.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 2041. (d) Glueck, D. S.; Hollander, F. G.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2719. (e) Rau, M. S.; Krets, C. M.; Mercando, L. A.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1991**, *113*, 7420.

[18] (a) The complexes $Cp^*Re(\eta^2\text{-}RC\equiv CR)OC(O)N(Ph)$ (R = Me, Ph) have also been spectroscopically characterized.[18b] Their reaction with phenyl isocyanate gave the corresponding ureato-*N,N′* complexes $Cp^*Re(\eta^2\text{-}RC\equiv CR)N(Ph)C(O)N(Ph)$, and the formation of an intermediate nitrene complex was proposed. Apparently the possibility of the CO_2 moiety remaining coordinated to the nitrene complex was not considered. This however, would explain why a "very efficient" back-reaction of the intermediate nitrene complex with the liberated CO_2 was observed, even in refluxing toluene, from which free CO_2 should be very quickly eliminated. (b) Herrmann, W. A.; Weichselbaumer, G.; Paciello, R. A.; Fisher, R. A.; Herdtweck, E.; Okuda, J.; Marz, D. W. *Organometallics* **1990**, *9*, 489.

[19] (a) After submission of this paper, Bergman *et al.* reported a zirconium complex[19b] containing a metallacyclic moiety composed of nitrene and olefinic fragments. An equilibrium between this complex and its isomer containing separate nitrene and coordinated olefin groups was proposed to explain the NMR data. (b) Walsh, P. J.; Hollander, F. J.; Bergman, R. G. *Organometallics* **1993**, *12*, 3705.

[20] Despite the fact that we could not even observe a nitroso complex under a range of conditions, it should be noted that in the FAB⁻ mass spectrum of 2 (derived from reaction 4), the most intense peak indeed corresponds to $[(CO)_2Rh(PhNO)]^-$. Therefore, this complex should not be regarded as intrinsically unstable, but only as very reactive in solution.

[21] Cenini, S.; Ragaini, F.; Pizzotti, M.; Porta, F.; Mestroni, G.; Alessio, E. *J. Mol. Catal.* **1991**, *64*, 179.

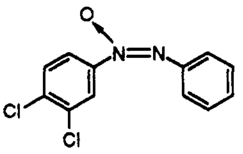
complex could not be isolated, since it decomposed rapidly to $[\mathrm{Rh_6(CO)_{15}}]^{2-}$ as the almost exclusively IR observable compound in solution. The formation of 3,4-dichloroaniline implies that in reaction 5 β-H elimination is not directly responsible for the amine formation. Since 1 was not re-formed when the possibility of an alcohol dehydrogenation was prevented, this experiment also suggests that this last process may, in any event, be involved in the reaction with methanol but that it occurs at a later stage than the production of the amine. Further evidence for the occurrence of alcohol dehydrogenation is given later in this paper.

Since methanol probably acts by protonating 3, we attempted to render this step irreversible by the use of methylating agents, as has already been done for other systems by Geoffroy *et al.*[22] Four different atoms are possible sites of attack for a proton: both of the oxygen atoms of the $\mathrm{CO_2}$ moiety and the oxygen and nitrogen atoms of the nitroso group. Although a rapid reaction was observed between 3 and $\mathrm{(CH_3)_3O^+BF_4^-}$ or $\mathrm{CH_3OSO_2CF_3}$ even at 0 °C, the intermediate complex underwent a series of further reactions, finally affording, when the reaction was conducted under a CO atmosphere, $\mathrm{Rh_4(CO)_{12}}$ as the only organometallic product. Aggregation of neutral carbonyl rhodium complexes not stabilized by bulky ligands is a common reaction. Although it was not possible to characterize the organic product of the decomposition, formation of $\mathrm{CO_2}$ was clearly observed during the first stage of the reaction. Thus, only the oxygen and nitrogen atoms of the nitroso moiety must be considered as possible protonation sites, but our data at this moment are not sufficient to distinguish between these.

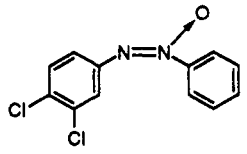
Reaction of $[\mathrm{PPN}][\overline{\mathrm{Rh(CO)_2ON(C_6H_3Cl_2)C(O)O}}]$ (3) with PhNO. When discussing the reaction of 1 with nitrosobenzene earlier in this paper, we reported some evidence for the formation of an intermediate nitrene complex and its competitive trapping by nitrosobenzene and methanol to afford, respectively, azoxybenzene and aniline. Since 3,4-dichloroaniline is the organic product arising from the reaction of 3 with methanol, a nitrene intermediate may also be formed in this case. To test this possibility, reaction 5 was performed in the presence of a 10-fold excess of nitrosobenzene (excess MeOH is also necessary to afford a reasonable rate, since no reaction at all occurs between 3 and PhNO in its absence). The formation of the mixed azoxybenzene $\mathrm{(3,4\text{-}Cl_2\text{-}C_6H_3)N{=}N(O)Ph}$ would be expected if a nitrene intermediate were formed.[23] The reaction proceeded smoothly at room temperature, and IR examination of the solution showed a gradual shift of the frequencies of the carbonyl bands from those of 3 to those of 2, but two different sets of peaks, one for each of the two compounds, could not be resolved. No other intermediate could be observed by IR spectroscopy during the reaction. When the products of the reaction were analyzed by gas chromatography–mass spectroscopy to identify the products) and gas chromatography (for quantitative analysis), an unexpected result was found. Two close but well-separated peaks were observed in the gas chromatogram, which showed in the mass spectrum the same parent peak at $M^+ = 266$ but different fragmentation patterns. This mass value corresponds to the mixed azoxybenzene, and the two species (4 and 5) were present in a relative amount of 1:1.77. Also present were tetrachloroazoxybenzene (0.25), dichloroaniline (0.18), tetrachloroazobenzene (0.04), and dichloroazobenzene (0.12), with the relative amounts with respect to 4 given in parentheses. The excess PhNO was catalytically converted to azoxybenzene as the largely dominant product, but some aniline and very small amounts of azobenzene and nitrobenzene were also found. Nitrobenzene was not contained as an impurity in the starting nitrosobenzene and thus must have been formed during the reaction.

Although we have made no attempt to optimize the conversion of nitrosobenzene to azoxybenzene, we point out that 1 is a much more active catalyst for this reaction than the complexes previously reported,[14,15] the reaction proceeding at room temperature in this case.

Two types of isomerism may explain the presence of the two asymmetric dichloroazoxybenzenes: positional isomerism (oxygen atom on the nitrogen atom bearing the substituted or the unsubstituted phenyl group) or *cis–trans* isomerism. The latter seems unlikely, since *cis* and *trans* isomers are expected to isomerize quickly under the conditions of the gas chromatographic analysis and only one peak is observed for all the other azo or azoxy compounds. In order to address this question, we synthesized both of the positional isomers by the method of Ōkubo and Koga.[24] Despite the fact that the two azoxy derivatives could not be obtained pure from other byproducts, each preparation clearly showed in its gas chromatogram only one of the two peaks corresponding to the mixed azoxybenzenes. This allows us to identify the first product (4) as $\mathrm{(3,4\text{-}Cl_2\text{-}C_6H_3)N(O){=}NPh}$ and the second, more abundant (5), as $\mathrm{(3,4\text{-}Cl_2\text{-}C_6H_3)N{=}N(O)Ph}$.[25]



4



5

In order for the presence of both 4 and 5 to be significant in the discussion below, it was necessary to ensure that they did not interconvert under the reaction conditions. Although 5 could be obtained only in very small amounts, 4 was obtained in higher yields, but even column chromatography was ineffective in removing some unreacted 3,4-dichloro-1-nitrobenzene. In order to ensure that none of the complexes intermediately formed during reaction 5 is able to promote the isomerization of an asymmetric azoxybenzene into the other and to avoid any uncertainty in the interpretation of the results due to possible reactions involving the free 3,4-dichloro-1-nitrobenzene, the following experiment was designed. The complex [PPN]-

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(22) For an example related to this field, see: Williams, G. D.; Whittle, R. R.; Geoffroy, G. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1987**, *109*, 3936.

(23) (a) Trapping of an intermediate nitrene complex to afford the symmetrical $\mathrm{{}^tBuN(O){=}N^tBu}$ has been reported previously.[23b] In the present case, however, formation of a symmetrical azoxybenzene would not be significant due to the large excess of free nitroso species necessary and the competitive reaction with methanol. (b) Pilato, R. S.; Williams, G. D.; Geoffroy, G. L.; Rheingold, A. L. *Inorg. Chem.* **1988**, *27*, 3665.

(24) Ōkubo, M.; Koga, K. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 203.

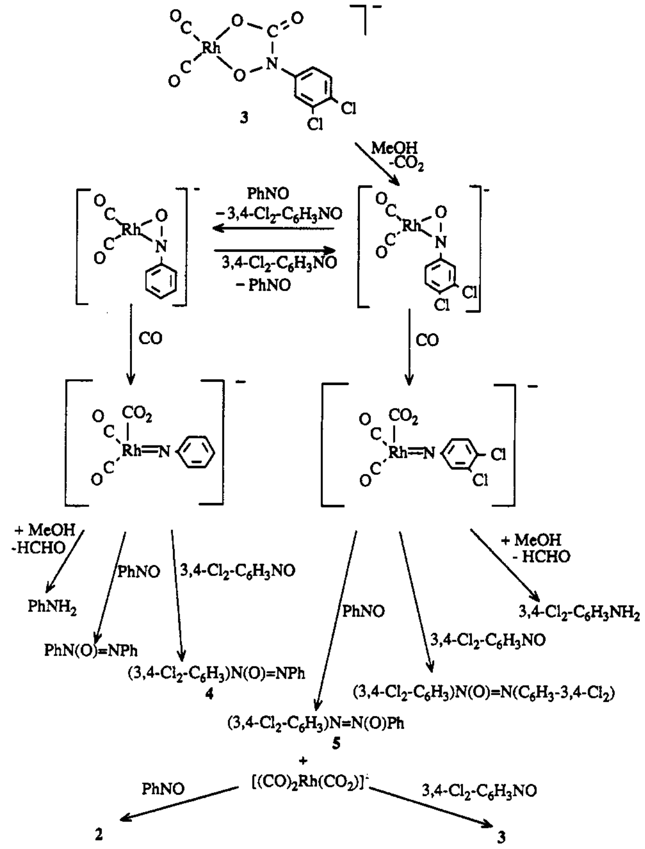
(25) The highest peak in the mass spectrum of both products corresponds to loss of the ON=NAr fragment: that is, 145 for 4 and 77 for 5. The $M^+ = 145$ peak was of very low intensity in the mass spectrum of 5, and the same is true for the $M^+ = 77$ peak in the mass spectrum of 4. This observation renders it easier to attribute the mass fragmentation pattern to a specific isomer in cases where the two compounds are not independently available.

$[\overline{\mathrm{Rh(CO)_2ON(C_6H_4\text{-}}o\mathrm{\text{-}CH_3)C(O)O}}]$ was generated *in situ* from 1 and a large excess of *o*-methylnitrosobenzene in THF under a CO atmosphere, and then the impure 4 was added. No reaction took place at this point. Methanol was then added, and the reaction was followed by gas chromatography–mass spectroscopy. If a direct isomerization of 4 (either metal-mediated or not) were possible, compound 5 should form. On the other hand, if a metathesis reaction involving the intermediate nitrene complex[26] were responsible for the formation of the two isomers, mixed azoxybenzenes containing either the methyl and the dichloro or the methyl and the unsubstituted moieties should be formed. While the first compound may also be derived from a reaction involving the 3,4-dichloro-1-nitrobenzene impurity, the second one definitely cannot. The reaction proceeded catalytically with respect to the conversion of the excess *o*-methylnitrosobenzene, and it was stopped when only a small quantity of this had remained. Analysis of the products showed that a small quantity of 4 had been reduced to the corresponding mixed azo compound, but most of it was still present. No other azo or azoxy compound was present, with the obvious exceptions of o-$\mathrm{CH_3\text{-}C_6H_4N(O){=}NC_6H_4}$-$o$-$\mathrm{CH_3}$ (which was the most abundant product) and some o-$\mathrm{CH_3\text{-}C_6H_4N{=}NC_6H_4}$-$o$-$\mathrm{CH_3}$ derived from its reduction. We had previously reported[3] that 1 is able to catalytically reduce azoxybenzene to azobenzene, although the reaction had been conducted under much more forcing conditions. Dichloronitrobenzene was apparently unaltered, and no dichloroaniline was present.

These results, taken together, clearly indicate that the two mixed azoxybenzenes 4 and 5 cannot arise from the isomerization of one into the other. Moreover, the absence of dichloroaniline or other products derived from dichloronitrobenzene, despite the fact that toward the end of the reaction the concentration of this last product is much higher than that of *o*-methylnitrosobenzene, points to the fact that a nitroso compound, even deactivated for both electronic and steric reasons, is in any case much more reactive than a nitro compound, even when the nitro compound is activated by electron-withdrawing substituents. This conclusion was not evident from the separate reactions of these two reagents with 1, since these are too fast to allow a comparison without a special apparatus for fast kinetics. The absence of the mixed azoxybenzene containing the methyl- and dichloro-substituted fragments among the products also suggests that an azoxy derivative can only be derived from a nitrene complex and a nitroso compound and not from a nitrene complex and a nitro compound.

Finally, it should be noted that no reaction took place between nitrosobenzene and 3,4-dichloroaniline or aniline under the same reaction conditions and in the absence of metal-containing species. It should also be stressed that we do not consider the above-mentioned experiments to constitute definitive proof that a nitrene complex, or its isomeric $\mathrm{CO_2}$–nitrene metallacycle, is an intermediate in the formation of the azoxybenzenes. However, on the basis of the data presented and in comparison with other known systems, other possibilities are either excluded or viewed as unlikely.

Scheme 3



Scheme 3 accounts for all of the products observed, except for the reduction of the azoxybenzenes to the corresponding azobenzenes. Some of the steps are common to Scheme 1 and were discussed earlier. At the end of the reactions in Scheme 3, 2 and 3, with a prevalence of the former, are formed and will reenter the same (for 3) or a similar (for 2) cycle.

The exchange of free and coordinated nitroso ligands seems a likely explanation for the formation of the isomeric 4 and 5 during the reaction of 3 with PhNO. The hypothesis that nitroso compounds can be displaced from their intermediate complexes is also consistent with the notion that azoxybenzene is actually formed during catalytic reactions[3] when no free nitrosobenzene has been added. It is possible that, at high pressures, CO may act as a displacing agent, in addition to being used as a reductant. Easy displacement of ^{t}BuNO from $\mathrm{(PEt_3)_2}$-$\mathrm{Ni(^tBuNO)}$ to yield the free nitroso compound and $\mathrm{(PEt_3)_2}$-$\mathrm{Ni(CO)_2}$ has been reported to occur simply upon bubbling CO into a solution of the complex.[13] It should be noted that the aforementioned nickel nitroso complex is isoelectronic with our proposed rhodium nitroso complex.

This is the first time that good evidence has been reported for the intermediate formation of a nitrene complex during a carbonylation reaction of an organic nitro compound catalyzed by a mononuclear late-transition-metal complex. Nitrene cluster compounds have, on the other hand, often been observed when the same reaction is catalyzed by $\mathrm{Ru_3(CO)_{12}}$, and their behavior has been

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[26] (a) Although, to the best of our knowledge, a metathesis reaction of a nitrene complex with an azo or azoxy compound to yield a different azo or azoxy compound has never been reported, it should be considered a possible reaction, since metathesis of azo compounds with carbene complexes[26b,c] or with a coordinated CO[26d] and of nitrene complexes with aldehydes[26e] have been reported. (b) Hegedus, L. S.; Kramer, A. *Organometallics* **1984**, *3*, 1263. (c) Arndtsen, B. A.; Sleiman, H. F.; Chang, A. K.; McElwee-White, L. *J. Am. Chem. Soc.* **1991**, *113*, 4871. (d) Smieja, J. A.; Gozum, J. E.; Gladfelter, W. L. *Organometallics* **1987**, *6*, 1311. (e) Jolly, M.; Mitchel, J. P.; Gibson, V. C. *J. Chem. Soc., Dalton Trans.* **1992**, 1329.

studied.[27] In the field of mononuclear catalysts, two other metallacyclic complexes of ruthenium[12b,28] and palladium,[29] corresponding to different stages in the reduction of the nitro group, have been previously isolated and shown to be intermediates in the catalytic cycle. The question of the eventual formation of nitrene complexes during further reactions of the ruthenium and palladium complexes has not been addressed in the above-mentioned papers. Preliminary evidence, based on the same type of decomposition of the metallacycle in the presence of excess nitrosobenzene as reported for the rhodium metallacycle in this paper, shows that a nitrene complex may also be an intermediate in the case of ruthenium[30] and be at least in equilibrium with the reported metallacyclic structure in the case of palladium,[31] where, however, the isocyanate may also be formed directly from the metallacycle.

Aniline as an Intermediate in the Catalytic Cycle. In a recent very stimulating paper,[28] Gladfelter *et al.* reported good evidence that anilines are intermediates in the Ru(DPPE)(CO)$_3$-catalyzed carbonylation of nitrobenzene or substituted nitrobenzenes in the presence of alcohols to yield the corresponding carbamates. The carbamates are obtained by the attack of the anilines on an intermediate carboalkoxy complex (eq 6). The most important experiment to check that this model reaction is actually relevant to the catalytic cycle under normal operating conditions involved the catalyzed carbonylation of *p*-nitrotoluene in the presence of *p*-chloroaniline, to yield a mixture of the carbamates containing either a methyl or a chloro substituent on the ring. To check if a similar mechanism was operating in our system, we performed an analogous experiment. Our rhodium system also gave mixtures of the two different carbamates and anilines when the carbonylation of nitrobenzene was conducted in the presence of an equimolar amount of *p*-toluidine at 145 °C (eq 7). No exchange was observed between methyl phenylcarbamate and *p*-toluidine under the same experimental conditions even in the presence of 1 and bpy.[33]

$$\mathrm{Ru(DPPE)(CO)_2(COOMe)_2 + ArNH_2 \rightarrow ArNHCOOMe + MeOH + Ru(DPPE)(CO)_3} \quad (6)$$

$$\mathrm{PhNO_2} + p\text{-}\mathrm{CH_3\text{-}C_6H_4NH_2} \xrightarrow[\mathrm{MeOH/toluene,\ 145\ ^\circ C,\ }P_{\mathrm{CO}}\mathrm{\ =\ 60\ atm}]{\mathrm{1/bpy}} \mathrm{PhNHCOOMe} + p\text{-}\mathrm{CH_3C_6H_4NH_2} + p\text{-}\mathrm{CH_3\text{-}C_6H_4NHCOOMe + PhNH_2} \quad (7)$$

Aniline is thus formed as an intermediate during the carbonylation of nitrobenzene even when the [Rh(CO)$_4$]$^-$-based catalytic system is used and is only converted to the carbamate at a later stage. The conversion of aniline to the carbamate likely occurs by a mechanism similar to the one proposed for the previously mentioned ruthenium-catalyzed system.[28] The efficiency of this last reaction is not complete, however, and part of the aniline is found unaltered at the end of the reaction. This is a common problem in carbonylation reactions of nitrobenzene with a variety of catalytic systems[1] and has been found to be due to dehydrogenation of the alcohol. Though these data have not been collected by us, it is relevant to this study that Liu and Cheng have reported[2] the formation of 2-butanone when the carbonylation of nitrobenzene catalyzed by 1 under conditions similar to those used by us (although in the absence of bpy) was performed using 2-butanol instead of methanol. The amount of 2-butanone formed was very closed to a 1:1 molar ratio with the observed aniline. When ethanol or 1-butanol was used as an alcohol, the corresponding aldehyde was obtained at the end of the reaction, although its quantity was lower than that of aniline, due to following reactions of the aldehyde under the reaction conditions. When *tert*-butyl alcohol was used, which cannot dehydrogenate, no aniline was left at the end of the reaction.[34] Under the conditions of our study, we could not directly observe the formation of formaldehyde, but when the reaction was performed at 145 °C, a temperature at which the selectivity of the reaction is lower and more aniline is formed,[3] we did observe the formation of a very small amount of *N*-methylaniline (identified by GC–MS). This product is generally attributed to reaction of aniline with formal-

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(27) (a) Cenini, S.; Crotti, C.; Pizzotti, M.; Porta, F. *J. Org. Chem.* **1988**, *53*, 1243. (b) Cenini, S.; Pizzotti, M.; Crotti, C.; Porta, F.; La Monica, G. *J. Chem. Soc., Chem. Commun.* **1984**, 1286. (c) Han, S.; Song, J.; Macklin, P. D.; Nguyen, S. T.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1989**, *8*, 2127. (d) Basu, A.; Bhaduri, S.; Khwaja, H. *J. Organomet. Chem.* **1987**, *319*, C28.

(28) Gargulak, J. D.; Berry, A. J.; Noirot, M. D.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1992**, *114*, 8933.

(29) Leconte, P.; Metz, F.; Montreoux, A.; Osborn, J.; Paul, F.; Petit, F.; Pillot, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1616.

(30) [$\mathrm{\overline{Ru(DPPE)(CO)_2ON(C_6H_3Cl_2)C}(O)}$] (synthesized from Ru(DPPE)(CO)$_3$ and 3,4-Cl$_2$-C$_6$H$_3$-NO$_2$ analogously to report in refs 12b and 28; DPPE = 1,2-bis(diphenylphosphino)ethane) was heated at 55 °C in THF, under atmospheric pressure of CO, in the presence of methanol and of a 10-fold excess of PhNO. Analysis of the organic products showed again the presence of the two mixed azoxybenzenes 4 and 5, together with minor quantities of dichloroazobenzene, tetrachloroazobenzene, and dichloroaniline. The excess PhNO was catalytically converted mainly to azoxybenzene, but minor quantities of azobenzene and aniline were also found. During the synthesis of [$\mathrm{\overline{Ru(DPPE)(CO)_2ON(C_6H_3Cl_2)C}(O)}$] we observed the previously unreported rapid (*ca.* 5 min) formation of an intermediate complex showing in the IR spectrum (in toluene) two absorptions at 2028 (s) and 1952 (vs) cm^{-1}. Stirring the solution under a CO atmosphere overnight afforded the final product. Since CO$_2$ evolution is observed during the first minutes of reaction, we tentatively attribute these absorptions to an intermediate nitroso complex, Ru(DPPE)(CO)$_2$(3,4-Cl$_2$-C$_6$H$_3$NO), which then more slowly inserts a CO molecule into the Ru–N bond. Further studies are in progress to ascertain this attribution.

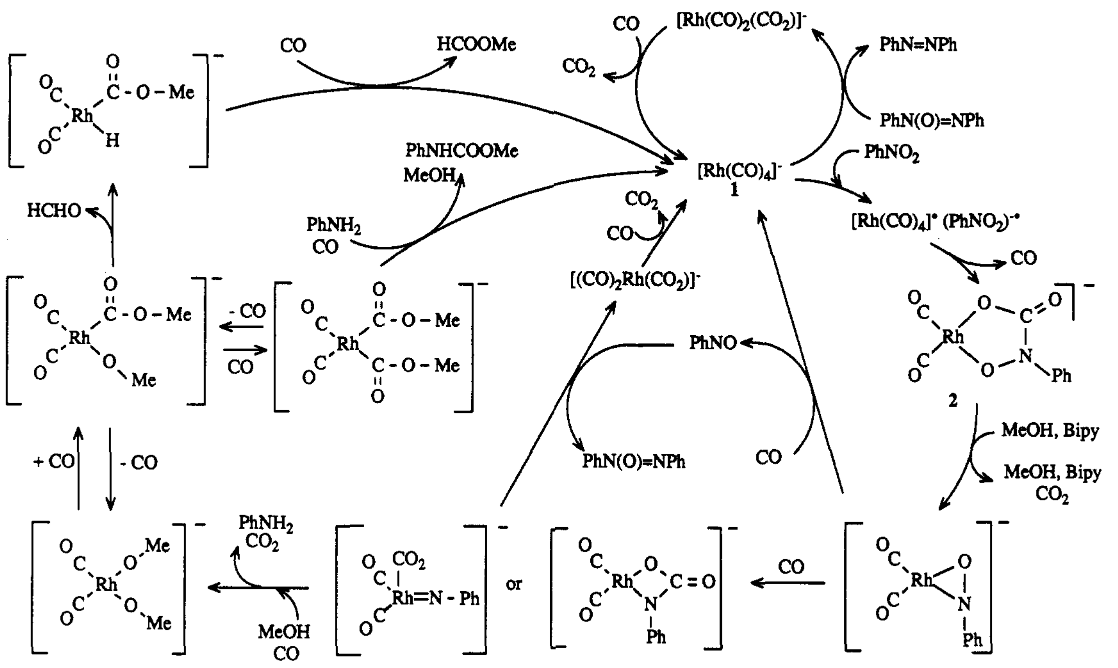
(31) $\mathrm{\overline{Pd(TMPhen)C(O)ON(}p\text{-}^i\mathrm{Pr\text{-}C_6H_4)C}\mathrm{(O)}$ (synthesized analogously to the method reported in ref 29; TmPhen = 3,4,7,8-tetramethyl-1,10-phenathroline) and a 10-fold excess of PhNO were heated to 170 °C in *o*-dichlorobenzene in an autoclave under 20 atm of CO. Analysis of the organic products showed the presence of the mixed azo compound p-^{i}Pr-C$_6$H$_4$N=NPh as the largely dominant product containing the substituted phenyl group. A very small quantity of p-^{i}PrC$_6$H$_4$NCO (identified by its reaction with MeOH to give the corresponding carbamate) was observed, but no mixed azoxy derivative was detected. The absence of the mixed azoxy derivative can likely be attributed to its reduction under the forcing reaction conditions. This type of reduction has precedent.[3] Also consistent with this explanation is the fact that the excess nitrosobenzene is catalytically converted mainly to azobenzene, but some azoxybenzene is also present. Although this experiment does not imply that a nitrene complex is an intermediate in the production of the isocyanate, which is already present as a fragment of the metallacyclic complex and may be directly eliminated from that, it shows that such a complex is at least in equilibrium with the reported metallacycle. Decarbonylation of a coordinated isocyanate ligand (proposed to yield a nitrene complex) has been observed in the case of the somewhat related complex Ni(PPh$_3$)$_2$(PhNCO).[32] Further studies are in progress to better understand this reaction.

(32) Hoberg, H.; Korff, J. *J. Organomet. Chem.* **1978**, *335*, C20.

(33) When the catalytic experiment was conducted at the more commonly employed temperature of 200 °C, the same result was observed. However, complete exchange of methyl phenylcarbamate with toluidine to yield a mixture of all of the two possible carbamates and anilines occurred in the control experiment.

(34) (a) In a previous study, one of the same authors had reported that, in the absence of CO, various rhodium compounds catalyze the transfer hydrogenation of nitrobenzene by secondary alcohols. Under the conditions of this last study, the formation of aniline and of the ketone becomes, in some cases, quantitative.[34b] (b) Liou, K. F.; Cheng, C. H. *J. Org. Chem.* **1982**, *47*, 3018.

Scheme 4



dehyde, followed by reduction of the resulting imine.[35] At the end of this reaction, we also detected the formation of a small amount of methyl formate. In the course of a preliminary high-pressure IR study we could also observe this product (ν_{CO} 1739 cm^{-1}) in solution under the same conditions used in catalysis but in the absence of nitrobenzene.[36] The formation of methyl formate is in accord with the presence in solution of a carbomethoxy complex and with the previously proposed β-hydrogen elimination from a coordinated methoxy group (see also Scheme 4).

Although the involvement of aniline as an intermediate is sufficient to explain why only a very poor conversion with a low selectivity for isocyanate is observed under normal catalytic conditions but in the absence of methanol,[3] another explanation may also be proposed. Insertion of CO into a metal–nitrene bond to afford the isocyanate may be reversible. Thus, in the absence of a compound such as methanol, which can trap the formed isocyanate to afford an unreactive carbamate, an equilibrium may be established and the reaction would not proceed further. The reaction of $Ru_3(CO)_{12}$ with PhNCO to give the nitrene cluster $Ru_3(CO)_{10}(\mu_3\text{-NPh})$ has been reported,[37] and its occurrence may explain why conversion of nitrobenzene to phenyl isocyanate is difficult to obtain catalytically with this cluster, despite the fact that a stoichiometric reaction has been obtained in a model study under very mild conditions.[27c]

To check if this was the case in the system examined here, we performed the reaction of 1 with excess PhNCO in THF under a dinitrogen atmosphere. Quite unexpectedly we found that 1 catalytically converts PhNCO to its trimer even at room temperature (eq 8). Complex 1 was

$$\text{PhNCO} \xrightarrow[\text{THF, room temp, N}_2]{1} (\text{PhNCO})_3 \qquad (8)$$

found unaltered at the end of the reaction. Intermediate coordination of the isocyanate to rhodium can be excluded, since this would require the loss of a CO group which could not be later replaced. Thus, 1 is apparently acting only as a base. Base-catalyzed oligomerization of isocyanates is a known reaction.[38] To the best of our knowledge, only in one other case has the cyclotrimerization of PhNCO been reported to be catalyzed by a metal carbonyl complex.[39] However, CO loss was clearly necessary for the reported complex to be active. In any case, reaction 8 is clearly inconsistent with the hypothesis of a reversible carbonylation reaction of the intermediate nitrene complex.

Conclusions

In this paper, we have reported a mechanistic study on the $[Rh(CO)_4]^-$/nitrogen base catalytic system for the carbonylation of nitrobenzene to methyl phenylcarbamate. A comprehensive picture of all the proposed steps is given in Scheme 4.

Although many of the proposed intermediates have proven to be too reactive to allow isolation or even observation, indirect evidence for their involvement in the catalytic cycle has been given. In particular intermediate 2 has been isolated and its analogue, 3, was crystallographically characterized. The reactions of 1 with nitro and nitroso aromatic compounds have been shown to involve an electron-transfer process. Reaction of 3 with methanol in the presence of nitrosobenzene constitutes good evidence for the formation of a nitrene complex, and the formation of the isomeric asymmetric azoxybenzene is best explained by the proposed intermediate formation of a nitroso complex. The use of nitrosobenzene as a trapping agent for reactive nitrene complexes, especially

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[35] (a) Reference 35b and references therein. Using a ruthenium-based catalyst, the authors of this study also detected the presence of $PhN{=}CH_2$. (b) Gargulak, J. D.; Hoffman, R. D.; Gladfelter, W. L. *J. Mol. Catal.* **1991**, *68*, 289.

[36] Ragaini, F.; Cenini, S. Work in progress. In the presence of nitrobenzene, the absorption for methyl formate is obscured by the much more intense absorption of methyl phenylcarbamate, which appears at almost exactly the same frequency. The formation of methyl formate has also been previously reported by Gladfelter *et al.* in a system related to this.[35b]

[37] Sappa, E.; Milone, A. *J. Organomet. Chem.* **1973**, *61*, 383.

[38] Tiger, R. P.; Sarynina, L. I.; Entelis, S. G. *Russ. Chem. Rev.* (*Engl. Transl.*) **1972**, *41*, 774.

[39] Martelli, E.; Pelizzi, C.; Predieri, G. *J. Mol. Catal.* **1983**, *22*, 89.

if they bear groups different from the unsubstituted phenyl, has proved to be a very promising reaction for applications to other catalytic systems. Evidence for the formation of a CO_2 complex comes from the synthesis of **2** from nitrosobenzene. The role of aniline as an intermediate has also been proved. This leads to the proposal of a carboalkoxy intermediate, which is also in accord with the observed formation of methyl formate. Evidence for the competitive decomposition pathways for the carboalkoxy intermediate, apart from the aforementioned formation of methyl formate, comes from the previously reported[2] formation of 2-butanone when 2-butanol was used in place of methanol with the same catalytic system used in this study and from the detection of *N*-methylaniline.

Further studies are in progress to better confirm all the proposed steps and intermediates.

Experimental Section

General Procedure. Unless otherwise noted, all reactions and manipulations were performed under a dinitrogen atmosphere, using standard Schlenk apparatus. All solvents were dried, distilled, and stored under dinitrogen before use. Nitrobenzene was washed with 10% H_2SO_4, dried over $CaCl_2$, distilled under reduced pressure of dinitrogen, and stored under dinitrogen. All other organic reagents, except for **4**, were commercial products and were used as received. [PPN][Rh(CO)$_4$][40] and $Rh_4(CO)_{12}$[41] were synthesized by methods reported in the literature. [PPN][Rh(CO)$_4$] and the metallacyclic compounds **2** and **3** synthesized in this work are very air sensitive even in the solid state and should never be allowed to come into contact with air even for short periods of time. Weighing of these compounds must be performed under an inert atmosphere. Gas chromatographic analyses were conducted on a Perkin-Elmer 8420 gas chromatograph equipped with a PS 255 capillary column. For the purpose of quantitative analysis, hexamethylbenzene was used as an internal standard. Whenever possible, R_f values were determined by the use of solutions of known concentrations of the compounds. For the few cases in which the compound was not available in large amounts in a pure state (mixed azo and azoxy compounds), an approximate R_f was estimated by comparison of the measured R_f values for the unsubstituted azo- and azoxybenzene, nitrobenzene, and aniline with those of dichloronitrobenzene and dichloroaniline. Gas chromatographic–mass spectroscopic analyses were conducted on a Hewlett-Packard 5890 gas chromatograph equipped with a 5971 A mass selective detector. IR spectra were recorded on a Bio-Rad FTS-7 FT-IR spectrophotometer. EPR spectra were recorded on a Varian E109 ESR spectrometer, operating in the X band (9 GHz). Elemental analyses were performed by the Analytical Laboratories of Milano University.

Attempted Reactions of [PPN][Rh(CO)$_4$] (1) with bpy. (a) [PPN][Rh(CO)$_4$] (100 mg, 0.133 mmol) and bpy (208 mg, 1.33 mmol) were placed in a Schlenk tube under dinitrogen, and the solvent (THF, acetone, toluene, or dichlorobenzene, 5 mL) was added. The solution was heated to reflux. After 2 h no reaction was observed in the case of THF and acetone. The toluene solution afforded complete decomposition to an insoluble black material, which is proposed to be metallic rhodium on the basis of the absence of any absorption in the IR spectrum in the region 4000–400 cm^{-1}. The dichloromethane solution afforded within 10 min a yellow solution displaying two sharp absorption bands in the IR spectrum at 2055 and 1975 cm^{-1}. These bands were attributed to [PPN][RhCl$_2$(CO)$_2$] by comparison with those displayed by an independently prepared sample.[42]

(b) [PPN][Rh(CO)$_4$] (100 mg, 0.133 mmol), bpy (208 mg, 1.33 mmol), and THF (10 mL) were placed in a glass liner inside a Hastelloy autoclave with a procedure analogous to the one previously reported for the catalytic reactions.[3] CO (60 atm) was added, and the autoclave was heated at 200 °C for 1.5 h. At the end of the reaction an IR spectrum of the solution evidenced the presence of $Rh(CO)_4^-$ (ν_{CO} 1896 cm^{-1}) and other lower intensity absorptions at 2061 (w), 2039 (w), 2016 (s), 1820 (m), and 1725 (w) cm^{-1} indicative of one or more cluster compounds. To this solution was added $PhNO_2$ (327 mg, 273 μL, 2.66 mmol), and the reaction was monitored by IR spectroscopy. Complete disappearance of $Rh(CO)_4^-$ was observed in 6 h. During the same time only a small decrease in the intensity of the other absorptions was noticed.

Synthesis of [PPN][$\overline{\text{Rh(CO)}_2\text{ON(C}_6\text{H}_5\text{)C(O)O}}$] (2). (a) From 1 and PhNO. **1** (200 mg, 0.266 mmol) and PhNO (85.5 mg, 0.798 mmol) were placed in a Schlenk tube under a dinitrogen atmosphere, and THF (5 mL) was added. An immediate reaction occurred upon dissolution. A black solution was obtained, displaying in the IR spectrum only the signals of **2** (see text) and a small absorption at 1672 cm^{-1}.[6] Hexane (20 mL) was added, affording a black tarry precipitate and a clear solution. Gas chromatographic analysis of the solution evidenced the presence of (percentage molar amounts in parentheses): azoxybenzene (89), azobenzene (1.5), aniline (5), nitrobenzene (3), and unreacted nitrosobenzene (1.5). The black tarry material was dried *in vacuo* and washed with more hexane until it became a powder. A FAB$^-$ mass spectrum of this solid showed a parent peak at $M^- = 310$, consistent with the proposed formulation for **2**, and peaks corresponding to the loss of CO_2 (most intense peak) and two CO groups. Consistent elemental analyses could not be obtained for this material, which decomposed during any attempt at purification.

(b) From 1 and PhNO$_2$. **1** (200 mg, 0.266 mmol) was placed in a Schlenk tube and dissolved in THF (5 mL), and $PhNO_2$ (327 mg, 273 μL, 2.66 mmol) was added. The solution was heated at 40 °C for 2 h, at the end of which time **1** had been completely consumed and only the absorptions due to **2** (see text) were observed in the IR spectrum. Workup of the black solution was performed as reported for the synthesis employing PhNO. Even in this case consistent elemental analyses could not be obtained.

Synthesis of [PPN][$\overline{\text{Rh(CO)}_2\text{ON(C}_6\text{H}_3\text{Cl}_2\text{)C(O)O}}$] (3). **1** (300 mg, 0.40 mmol) was placed in a Schlenk tube under a CO atmosphere, and THF (6 mL) was added. The solution was stirred for 15 min to allow for saturation by CO. 3,4-Cl_2-$C_6H_3NO_2$ (84.5 mg, 0.44 mmol) was then slowly added, and the solution was stirred for 10 min, after which time an IR spectrum showed, in the carbonyl region, only the absorptions attributed to **3** (2050 (s), 1973 (vs), 1638 (m) cm^{-1}). When in solution and under a CO atmosphere, **3** is exceedingly sensitive to moisture. Any water present, even in traces, will react with **3** to yield 3,4-dichloroaniline and regenerate **1** (see the analogous reaction with methanol). In this eventuality, addition of more dichloronitrobenzene may be necessary to consume also the re-formed **1**. To the black THF solution, hexane was added drop by drop until a black tarry precipitate was formed and the solution became yellow (*ca.* 2 mL). Care should be taken during this operation, since addition of too little hexane will afford an impure product, while even a few drops more will cause the isolated yield to drop. The yellow solution was transferred to another Schlenk tube, and more hexane (20 mL) was added. This caused the precipitation of **3**·THF as a yellow, crystalline material, which was filtered off, washed with more hexane, and dried *in vacuo* (292 mg, 74% isolated yield). ^{13}C NMR (THF-d_8): δ 188 (d, $J_{Rh-C} = 42$ Hz, CO), 189 (d, $J_{Rh-C} = 57$ Hz, CO), 145 (s, CO_2). The signals of the phenyl group were shielded by the more intense signals of the PPN^+ countercation. Anal. Calcd for $C_{49}H_{41}N_2Cl_2O_6P_2Rh$: C, 59.5; H, 4.2; N, 2.8. Found: C, 59.2; H, 4.0; N, 2.8. When perfectly

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[40] (a) Garlaschelli, L.; Chini, P.; Martinengo, S. *Gazz. Chim. Ital.* **1982**, *112*, 285. (b) Garlaschelli, L.; Della Pergola, R.; Martinengo, S. *Inorg. Synth.* **1990**, *28*, 211.

[41] Martinengo, S.; Giordano, G.; Chini, P. *Inorg. Synth.* **1990**, *28*, 242.

[42] Forster, D. *Inorg. Nucl. Chem. Lett.* **1969**, *5*, 433.

pure, the compound is indefinitely stable in the solid state under a dinitrogen atmosphere.

Reaction of [PPN][$\overline{Rh(CO)_2ON(C_6H_3Cl_2)C(O)O}$] (3) with MeOH/CO or MeOH/CO/bpy. In order to avoid any uncertainty due to the limited accuracy in the weight measurements of small quantities of compound under dinitrogen, the following procedure was adopted: **3**·THF (100 mg, 0.10 mmol) was placed in a Schlenk tube under a CO atmosphere and dissolved in THF (6 mL). MeOH (40 μL) was then added, and half of the solution was quickly transferred to another identical Schlenk tube connected to the same CO line. bpy (24 mg, 0.15 mmol) was then immediately added to the second Schlenk tube. Both of the tubes contained a magnetic bar of the same dimension and were stirred with the same magnetic stirrer. The parallel reactions were followed by IR spectroscopy. In both of the cases, a gradual decrease in the intensity of the absorptions of **3** and a parallel increase in the intensity of the absorption of **1** were observed. No intermediate was observable, and only some very weak absorptions not belonging to **1** were present in the carbonyl region of the IR spectra at the end of the reaction. The reaction in the presence of bpy was faster and was complete in 2.5 h, whereas the other required about 6 h before all of **3** had been consumed. No induction period was observed for either of the reactions. At the end of the reaction the intensity of the 1896 cm^{-1} absorption due to **1** was virtually identical for the two solutions, proving that no complex containing bpy but not CO is formed in the second solution. Hexane (10 mL) was added to both of the solutions. The resulting solutions, only containing the organic products of the reaction, were analyzed by gas chromatography. $3,4\text{-}Cl_2C_6H_3NH_2$ and bpy (only for the second solution) were the only detectable products. The same type of procedure was used to compare the accelerating effect on this reaction of bpy and of a double molar amount of pyridine. However, in this case no appreciable difference was observed in the rate of the two reactions.

Reaction of [PPN][$\overline{Rh(CO)_2ON(C_6H_3Cl_2)C(O)O}$] (3) with bpy. **3**·THF (50 mg, 0.05 mmol) and bpy (24 mg, 0.15 mmol) were placed in a Schlenk tube under a dinitrogen atmosphere, and THF (3 mL) was added. The reaction proceeded slowly, and about 15 h was necessary for **3** to be completely consumed. At the end of the reaction no carbonyl-containing product was present in the solution and a black non-carbonyl-containing precipitate was formed. Gas chromatographic analysis of the solution evidenced the presence of bpy and of a very small amount (*ca.* 4% relative to bpy) of 3,4-dichloroaniline.

Reaction of [PPN][$\overline{Rh(CO)_2ON(C_6H_5)C(O)O}$] (2) with MeOH/CO under High Pressure. THF (6 mL) and MeOH (2 mL) were placed in a glass liner inside an autoclave with the same procedure used for catalytic reactions.[3] CO (60 atm) was added, and the autoclave was heated at 200 °C. An impure sample of **2** (100 mg), prepared by reaction of **1** with PhNO as previously described, was dissolved in THF (2 mL) and the solution added to the hot THF/MeOH solution by means of a high-pressure side reservoir. Heating was continued for 15 min, after which time the autoclave was cooled with an ice bath. Gas chromatographic analysis of the solution evidenced the presence of aniline and methyl phenylcarbamate in an approximately 4:1 molar amount. Neither of these two products was present as an impurity in the starting **2**.

Synthesis and Characterization of $3,4\text{-}Cl_2C_6H_3N{=}N(O)\text{-}Ph$ (4) and $3,4\text{-}Cl_2C_6H_3N(O){=}NPh$ (5). $(3,4\text{-}Cl_2\text{-}C_6H_3)N\text{-}(O){=}NPh$ (**4**) and $(3,4\text{-}Cl_2\text{-}C_6H_3)N{=}N(O)Ph$ (**5**) were synthesized by a modification of the method reported in ref 24. **5** was not isolated and was characterized only by gas chromatography–mass spectroscopy. **4** was purified from all other byproducts except some $3,4\text{-}Cl_2\text{-}C_6H_3NO_2$ by column chromatography (eluent CH_2Cl_2/hexane 1:1). High-resolution mass: 266.0022 (calcd 266.0014). The isotopic peak at $M^+ = 268$ had intensity 0.650 with respect to the $M^+ = 266$ peak (calcd 0.660). From the same chromatographic separation a very small amount of not perfectly pure $3,4\text{-}Cl_2C_6H_3N{=}NPh$ was obtained. High-resolution mass: 250.0074 (calcd 250.0065). The isotopic peak at $M^+ = 252$ had intensity 0.661 with respect to the $M^+ = 250$ one (calcd 0.657).

Reaction of [PPN][$\overline{Rh(CO)_2ON(C_6H_3Cl_2)C(O)O}$] (3) with PhNO/MeOH/CO. **3**·THF (100 mg, 0.10 mmol) and PhNO (107 mg, 1.0 mmol) were placed in a Schlenk tube under a CO atmosphere and dissolved in THF (4 mL). No reaction was observed at this stage over 30 min. MeOH (40 μL) was then added and the reaction monitored by IR spectroscopy and gas chromatography–mass spectroscopy. To avoid the injection of metal-containing solutions into the gas chromatograph, 0.5 mL samples of the reacting solution were withdrawn and were treated with hexane (1 mL). This afforded complete precipitation of the anionic complexes, whereas all the organic compounds remained soluble. These solutions were injected into the gas chromatograph without any further workup. The results of this experiment have already been described in the Results and Discussion.

Attempted Isomerization of $(3,4\text{-}Cl_2\text{-}C_6H_3)N(O){=}NPh$ (4). [PPN][Rh(CO)$_4$] (**1**; 50 mg, 0.066 mmol) was placed into a Schlenk tube under a CO atmosphere and dissolved in THF (4 mL). $o\text{-}CH_3\text{-}C_6H_4NO$ (121 mg, 1.0 mmol) was then added. [PPN][$\overline{Rh(CO)_2ON(C_6H_4\text{-}o\text{-}CH_3)C(O)O}$] was immediately formed, as evidenced by IR spectroscopy (ν_{CO} 2040 (s), 1960 (vs), 1626 (m) cm^{-1}). A small band[6] was also observed at 1672 cm^{-1}. The impure sample of **4** (50 mg, also containing approximately 30% $3,4\text{-}Cl_2\text{-}C_6H_3NO_2$) dissolved in THF (1 mL) was then added. No reaction was observed during 30 min. Methanol (50 μL) was then added, and the reaction was monitored as described for the previous reaction. The results of this experiment have already been described in the Results and Discussion.

Reaction of [PPN][$\overline{Rh(CO)_2ON(C_6H_3Cl_2)C(O)O}$] (3) with $p\text{-}CH_3\text{-}C_6H_4OH$. **3**·THF (100 mg, 0.1 mmol) was placed in a Schlenk tube under a CO atmosphere and dissolved in THF (5 mL). $p\text{-}CH_3\text{-}C_6H_4OH$ (108 mg, 1.0 mmol) was then added. After 10 min, the IR spectrum showed that the starting metallacycle had been completely consumed. Two strong carbonyl bands were observed in the IR spectrum at 2053 and 1977 cm^{-1}, but various other very weak absorptions were present. Formation of CO_2 was clearly observed by IR. The appearance of the IR spectrum immediately started to change when the solution was let stand. After 30 min the initially formed complex was no longer present and the solution contained $[Rh_6(CO)_{15}]^{2-}$ as the largely dominant product, as evidenced by comparison of the IR spectrum of the solution with that of an authentic sample.[43] Gas chromatographic analysis of the solution evidenced the presence of 3,4-dichloroaniline as the only observable organic product.

Methylation of [PPN][$\overline{Rh(CO)_2ON(C_6H_3Cl_2)C(O)O}$] (3) with $CH_3O_3SCF_3$. **3**·THF (100 mg, 0.10 mmol) was placed in a Schlenk tube under a CO atmosphere and dissolved in CH_2Cl_2 (4 mL) at 0 °C. $CH_3O_3SCF_3$ (16.4 mg, 11.3 μL, 0.10 mmol) was then added with a microsyringe, and the solution was stirred at 0 °C. An immediate reaction occurred, leading to the formation of CO_2 (as evidenced by IR spectroscopy) and of a complex showing in the IR spectrum two bands at 2062 and 1994 cm^{-1}, indicative of a neutral, *cis*-dicarbonyl complex. However, the appearance of the IR spectrum of the solution immediately started to change and, after 2 h, almost the only complex present in solution was $Rh_4(CO)_{12}$[41] (as evidenced by a comparison of its IR spectrum with that of the pure compound). A similar procedure was employed when $(CH_3)_3OBF_4$ was used as a methylating agent instead of $CH_3O_3SCF_3$. Attempts to isolate the intermediately formed complex by working under a nitrogen atmosphere, instead of a CO one, or by chilling the solution at −80 °C after the first step was completed did not meet with success.

Catalytic Reactions. Cataytic reactions were conducted as already described in a preceding paper.[3] In order to detect the

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(43) Martinengo, S.; Chini, P. *Gazz. Chim. Ital.* **1972**, *102*, 344.

(44) North, A. C.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr.* **1968**, *A24*, 351.

formation of methyl formate, a run was conducted under the same concentration conditions as the ones reported in Table 4, but at 145 °C for 3 h. At the end of the reaction the autoclave was cooled at room temperature with a water bath and the venting valve was connected to an empty bubbler. The bubbler was cooled to approximately −40 °C and the autoclave was vented. The condensed vapors were subjected to GC–MS analysis, which evidenced the presence of a small amount of methyl formate.

X-ray Data Collection and Structure Determination. Crystal data and other experimental details are summarized in Table 1. A prismatic crystal with approximate dimensions 0.10 × 0.08 × 0.18 mm was used. The diffraction measurements were carried out on a Enraf-Nonius CAD4 diffractometer at room temperature, using graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). The diffracted intensities were corrected for Lorentz, polarization, and absorption (empirical correction[44]), but not for extinction. Scattering factors for all the atomic species and anomalous dispersion corrections for scattering factors of non-hydrogen atoms were taken from ref 45. The structure was solved by Patterson and Fourier methods and refined by full-matrix least squares, minimizing the function $\sum w(|F_o| - k|F_c|)^2$. An anisotropic thermal parameter was assigned to all the non-hydrogen atoms. The hydrogen atoms were introduced in the structure model at calculated positions (C–H = 0.95 Å); no refinement was attempted for these atoms. The final difference Fourier synthesis showed maxima residuals of 0.8 e/Å^3. The atomic coordinates are listed in Table 2. All the calculations were performed on a PDP11/73 computer using the SDP-Plus Structure Determination Package.[46]

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Supplementary Material Available: Structural data for **3**, including lists of calculated positions for the hydrogen atoms, anisotropic thermal parameters, and interatomic distances and angles (11 pages). Ordering information is given on any current masthead page.

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